PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Sunil Madhukar Bhangale, et al.

Serial No.: 10/512,113

Filed: October 21, 2004

For: METHOD FOR ELECTROLESS DEPOSITION OF A METAL LAYER ON SELECTED PORTIONS OF A SUBSTRATE

Examiner: Chacko Davis, Daborah

Group Art Unit: 1795

Attorney Docket No.: 3110.ARTH.PT

Declaration Under 37 CFR 1.131

Commissioner For Patents
P. O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

We, Sunil Madhukar Bhangale, Zhongli Li, and Peter Malcolm Moran, declare that:

1. We are each over twenty-one years of age and competent to give sworn testimony.

2. We are the named inventors in United States Patent Application Serial No. 10/512,113 entitled "METHOD FOR ELECTROLESS DEPOSITION OF A METAL LAYER ON SELECTED PORTIONS OF A SUBSTRATE METHOD FOR CHARGING

EFFLORESCENT MATERIAL USING ULTRAVIOLET LIGHT" filed on 21 October 2004 as National Stage Entry of International Application No. PCT/SG2003/000093 filed on 23 April 2003 and claiming priority to Singapore Patent Application No. SG 200202366-1 filed on 23 April 2002.

3. Attached as Exhibit A hereto is an invention disclosure form we completed on 17 April 2001, for the invention claimed in the above-identified patent application, then referred to as Novel patterning method for selective metallization.

4. As stated on page number 2 of the invention disclosure form, we conceived of the invention on or about October 1999.

5. Prior to the conception of the present invention, we were aware of difficulties in selectively seeding surfaces for electroless metallization, specifically the difficulties in ensuring that only desired portions of a surface are seeded. As we believed the present invention would address these difficulties we diligently worked to develop and test the processes of the present invention, as outlined in the pages numbered 4 though 7 of the invention disclosure form and the results shown in the microscope images of Figures 1 through 5 of the invention disclosure form, through the 17 April 2001 date of such form.

6. Following, 17 April 2001, we continued to diligently work on these processes, performing additional experimentation and assisting with the preparation of the Singapore Patent Application No. SG 200202366-1 which was filed on 23 April 2002, and the preparation of the present patent application.

7. Based on the foregoing, we were in possession of our invention as claimed in the present application prior to November 29, 2001, the filing date of the application which matured into U.S. Patent 6,498,087 to French et al. and is the parent application of the divisional patent application published as U.S. Patent Application Publication

2003/0034525, which was filed October 7, 2002.

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the patent.

Date: 15. Dec. 2008

Sunil Madhukar Bhangale

Date: 10. Dec. 2008

Zhongli Li

Date: 9 December 2008

Peter Malcolm Moran

EXHIBIT A

CONFIDENTIAL

INSTITUTE OF MATERIALS RESEARCH AND ENGINEERING

INSTITUTE OF MATERIALS RESEARCH AND ENGINEERING
3, Research Link, SINGAPORE 117 602

NOTE TO INVENTORS

The purpose of this form is to inform the Intellectual Property (IPR) Committee ~~of your invention/technology~~ when something new and useful has been conceived and developed, or when unusual, unexpected or non-obvious research results have been achieved and can be of commercial relevance, impact or importance to the institute.

For an invention disclosure to be patentable, an invention must be judged to satisfy three criteria:

1) **Novelty** – to be patentable, an invention must be "new". Even though an invention disclosure is new to the inventor, it is not patentable if another inventor made the same discovery earlier. If it has been used or sold, known by others, previously patented, disclosed in a printed publication, or in the public use, a new patent is barred.
2) **Utility** – the invention must be of some degree of use for some purpose that is not immoral.
3) **Non-obvious** – the invention must not be obvious to a person who has ordinary skill in the field of invention at the time the invention was made.

Please submit this disclosure to the Business Development Department in the enclosed form below, with the following items stated herein:
Title of the invention disclosed
Abstract/summary of the Invention
Detailed Statement of Invention and suggested scope
Carrying out the Invention
Claims
Background Art/Information
Uses of the Invention
Please note that publication or public disclosure would jeopardise any patent application. Any disclosure shall be disallowed till further notice from the IPR Committee or patent filing.

- *Kindly use Large Fonts to assist the drafters*
- *Kindly annex copies of relevant references to facilitate drafting*

SUPPORTING INFORMATION FOR IPR COMMITTEE (Attach additional sheets as necessary)

1. When did you first think of this invention?

October 1999

2. Where do you record this conception of ideas, e.g. IMRE intellectual logbook, notes, letters, memos, research proposals?

Unrecorded

3. To whom did you first disclose the invention, either orally or in writing. Specify the form of disclosure, such as verbal discussion, email or memos.

Undisclosed

4. Indicate the Project related to this invention.

Invention made while considering methods for the Polymer MEMS project (IMRE project code: 112021)

5. List as many as possible commercial applications of your technology/invention and list the industrial companies that have/may have interest in this invention and state whether contact has been initiated and at what stage. What do you envision as the product or salable item which would result from the invention.

Commercial applications include selective metallization of various substrates including metals, ceramics and polymers. In particular, selective metallization of indium-tin oxide (ITO) is immediately commercially relevant.

We have spoken with, among others, Hagen Klausmann the Manufacturing Engineering Manager from OSRAM Opto Semiconductors (part of the Siemens, Infineon, OSRAM group) responsible for introducing new processes to their Penang production facility. He together with Ewald Guenther (form Infineon but stationed at IMRE) is very interested in the technology and expressed an interest in collaborating to bring it to production, see the attached letter from Hagen Klausmann.

6. List any known competitive products and their manufacturers.

Many other companies use ITO. The only one who we know of that may be using a similar technique is Philips, however we have spoken with the person who developed the process for Philips and he said that they had not tried to use polymers to pattern the seeding particles.

7. Who funded the work that led to the invention? Pls fill in the appropriate blanks below:

- National Science & Technology Board, project name and code Polymer MEMS (121021)

8. Please indicate status and action required (you may tick more than one box)

- application to file for patent

CERTIFICATION PAGE

TITLE OF INVENTION

Novel patterning method for selective metallization.

Date: 17/4/01
Time: 2pm
Invention Disclosure No.:

PARTICULARS OF THE INVENTORS *(THE NAMES OF INVENTORS MUST BE LISTED ALPHABETICALLY WITH CAPITALISED SURNAMES)*

1. Name(underline surname): Sunil Madhukar BHANGALE
Home Address/tel: Blk 602, Clementi west st.1, #05-14, Singapore-120602
Citizenship: INDIAN Tel: 873 0586
Permanent Residence Status (if any): Singapore PR
Company: IMRE
Company Address/tel: 874 1986
Signature: Date: 17/04/01

2. Name(underline surname): LI Zhongli
Home Address/tel: Blk 703 Choa Chu Kang st.53, #10-60, Singapore 680703
Citizenship: Australian
Permanent Residence Status (if any): PR
Company: IMRE
Company Address/tel: 874 8042
Signature: Date: 17.04.01

3. Name (underline surname): Peter Malcolm MORAN
Home Address/tel: #04-08 Tower 3B, West Cove Condos, 10 West Coast Crescent, Singapore 128041
Citizenship: South African
Permanent Residence Status (if any): Not a Singapore PR
Company: IMRE
Company Address/tel: 874 8352
Signature: Date: 17/4/01

WITNESS(ES):
I certify that the invention has been explained to and is understood by me.

Name: MING LI
Home Address/tel: 100 NANYANG CRESCENT, #05-01, SINGAPORE
Signature: Date: 17/4/01

Name: Ewald Guenther
Home Address/tel: 210 Mt. Sinai Rise, S'pore, 1649122
Signature: Date: 17/4/01

INVENTION DISCLOSURE FORM

A) Describe the **particular problem the invention seeks to solve.**

The invention provides a method for **selectively** metallizing ceramic, metal or polymer substrates.

It is often difficult to selectively seed a surface for electroless metallization. The problem is that the seeding material sticks not only to the areas that require seeding but also to other areas. Therefore the user may need to "deactivate" certain regions after seeding (such as is described in US patent **4,824,693**)

Philips describes a method for selectively seeding indium-tin oxide (ITO) on glass substrates, European Patent **0 518 422 A2.** They use polymer-stabilized colloidal particles that selectively adsorb to the ITO, but do not adsorb to the glass substrate. However in their patent they describe only how to activate **all** the ITO on the surface they do not describe how to seed the ITO selectively, i.e. only seed certain portions of the ITO and not others. This is a very important problem since in most devices using ITO it is important that only certain portions of the ITO be metallized. We have discovered a method to achieve this.

B) Describe the **previous attempts to solve the problem and the limitations or deficiencies your invention overcomes in the state of the art.**

Previous attempts include the Philips research described in Section A, European Patent **0 518 422 A2** (1992). This patent achieves selective activation of ITO on glass (the colloidal seeding particles do not adsorb to clean glass). They also achieve good adhesion between the ITO and plated metal, however, they are not able to selectively pattern the ITO (i.e. pattern some ITO and leave other portions unplated on the microscale).

Another attempt is described in US patent **4,824,693.** Here the ITO and glass substrate is seeded using colloidal palladium stabilized with tin. Since the seeding is not selective some portions of the substrate must be "deactivated" using hydrogen fluoride (HF). Besides the additional process step of using HF, it also has the disadvantages of attacking both glass and ITO, i.e. undercutting and underetching may occur. Furthermore the adhesion between the plated metal and ITO is poor.

Our method overcomes these disadvantages by providing a completely additive and selective method of seeding and plating ***only certain portions*** of ITO on any substrate. This is achieved by using a mask that the particles do not adsorb onto. This allows simple, accurate patterning on the microscale.

(C) Details of the **complete description of the invention** (details should be similar to that of the methods and results sections of a publication).

Summary of the general process flow:

- A colloidal suspension of catalytic particles is prepared.
- The polymeric resist is used to mask (in the desired pattern) the surface of the substrate.
- The substrate is dipped into the colloidal suspension of catalytic particles.
- Immediately after dipping the substrate is rinsed with clean water.
- Generally the substrate is dried with flowing air or nitrogen and then further dried in an oven.
- The substrate is immersed in an electroless metallization bath until the desired thickness of metal is deposited on the surface. No metal deposition occurs on the mask since the seeding particles do not stick to it.
- After metallization the mask may be stripped from the substrate.

An example of the process is described in more detail below.

First a colloidal suspension of catalytic particles is prepared. The catalytic particles are formed primarily from catalytic metals such as palladium. They are stabilized using polymers, for example polyvinyl alcohol (PVA) or polyvinyl pyrrolidone (PVP). Polymer-stabilized catalytic particles such as these are described in

papers (e.g. H. Hirai, H. Chawanya and N. Toshima, *J. Macromol. Sci-Chem A12* (1978) 1117) and in a patent sited earlier, **EP 0 518 422 A2**

An example of how to prepare such a solution is as follows:

1. Dissolve 150mg of PVP (weight averaged molecular weight = 50,000, although it could be anywhere from 10,000 to about 500,000) in DI water.
2. Dissolve 150mg of $PdCl_2$ in 5.25ml of HCl (~37% pure).
3. Mix the PVP and Pd Cl_2 solutions together.
4. Slowly add 10ml – 35ml of hypophosphorous acid (H_3O_2P), 50% pure, to the solution.
5. Add DI water until the total volume of the solution is 1 litre.

The PVP stabilized palladium colloid solution (hereafter called the "Pd/PVP sol") is very stable and can be kept for over 1 year under normal conditions (working in air) without noticeable change. This is in contrast to similar solutions described in European Patent **0 518 422 A2** which need to be kept under nitrogen.

A clean substrate with an ITO film or ITO pattern on it surface is coated with a resist. The resist could be photosensitive, e.g. using a dry film resist such as Asahi Chemical's Sunfort resists or DuPont's Riston resists work particularly well. Alternatively the resist could be made from a variety of different polymers that the colloidal particles do not adhere to, e.g. some polycarbonate, fluorinated ploymers, cellophane, polyimide and acrylate based polymers. These polymers can be patterned using photoresists, a laser or using other means such as screening. A third method is to use a steric layer of polymer to protect certain areas. As an example if the clean substrate is dipped into a dilute solution of PVP (without any Pd), the PVP will adsorb to the surface and when the substrate is subsequently dipped into the Pd/PVP sol, the steric layer will prevent it from adhering. The steric layer can be patterned using the laser for example, however usually the steric layer needs to remain wet in order to remain effective.

Preferably a photoresistive material is used for the patterning. Patterning of the photoresist on the substrate surface follows known procedures. The uncovered areas of the substrate must be clean after patterning, i.e. there should not be residue of polymeric or organic material left on the surface. If the surface is not clean enough it may be cleaned using methods such as plasma or UV ozone cleaning.

The clean patterned substrate is then dipped into the Pd/PVP sol. Usually the substrate need only be dipped in the solution for a few seconds. Once the substrate is removed it is immediately rinsed thoroughly with DI water. Preferably the substrate is then dried with nitrogen or air and then placed in an oven to remove any remaining water. The substrate is then placed in an electroless-plating bath to plate up the desired thickness of metal on the exposed substrate surface. Since the Pd/PVP particles do not adhere to the resist, no plating occurs on the resist. The resist may be removed either before or after the plating step, preferably after.

Figures 1 - 3 show optical microscope pictures (at different magnifications) of electroless nickel selectively plated on ITO using an Asahi Sunfort dryfilm resist. The circular holes in the resist are about 125 μm in diameter. As can be seen from the figures the plating is very selective with no plating occurring on either the glass substrate or on the photoresist. All the exposed ITO is plated uniformly.

Figures 4 - 6 show optical microscope pictures (at different magnifications) of the substrates after the resist layer has been removed. Again the figures show the plating to be highly selective. The circular nickel features are about 125 μm in diameter.

(D) Describe the novel features of your invention and why they are significant.

The novel features of this invention is the discovery that polymer-stabilized colloidal particles do not adhere to certain polymeric materials, these polymeric materials can be used to pattern the particles on a surface, and thereby get selective plating.

This is a very important discovery since, unlike **EP 0 518 422 A2** that only describes selectivity between glass and ITO and provides no method of selectively patterning the ITO (generally users would like to metallize some but not all the ITO on the surface). This can also extend to patterning other materials, i.e.

not just ITO.

Also it allows selective patterning of ITO on polymeric substrates. Flexible polymeric substrates are being investigated for flexible OLED displays, I have tried some of the polymeric substrates (such as polycarbonates) that people are considering and the Pd/PVP sol does not seed the polymer substrate but does seed the ITO patterned on them.

(E) Describe the state of development (prototype, animal model or other research results).

I have succeeded in patterning roughly 100μm diameter circles and lines on an ITO film. This is the right size scale for the OSRAM OLED products that are being manufactured today.

The plating is completely selective between the ITO and the photoresist material as can be seen from the attached figures.

(F) Details of literature research on prior art leading to this invention.

Three patents were filed by Fokkink and coworkers from Philips using these kinds of polymer stabilized particles to selectively seed ITO (**EP 0 518 422 A2** and **US 5,384,154**) and glass surfaces (**EP 0 577 187 A1**). Patents **EP 0 518 422 A2** and **US 5,384,154** are essentially the same and refer only to the selectivity between glass (which the particles do not seed) and other materials. It states that the particles **do** seed photoresists – our invention claims the opposite, i.e. there are resists it **does not** seed. Patent **EP 0 577 187 A1** describes using silanes to attach the particles to glass surfaces, i.e. using them to seed and plate glass. It is not relevant to our invention.

Two patents refer to Fokkink's patents, both are Philips patents (**US 5,738,977** and **US 5,798,811**). Patent **US 5,738,977** refers only to patent **EP 0 577 187 A1** as a method for seeding glass substrates using silanes, and is not relevant to our invention. Patent **US 5,798,811** refers to patent **US 5,384,154** but does not state how this patent is relevant to it. It refers to selective electroless patterning using a polymeric mask, but does not disclose how this is done, nowhere in the patent does it refer to the method of seeding for the electroless patterning. As such it is not relevant to our invention.

To our knowledge no other patent before or after them describes using these kinds of particles for selective seeding.

Papers referring to the use of such polymer-stabilized catalytic particles include:

- H. Hirai, H. Chawanya and N. Toshima, *J. Macromol. Sci-Chem A12,* 1117 (1978).
- H. Hirai, *J. Macromol. Sci-Chem A13,* 633 (1979).
- E. P. Boonekamp, J. J. Kelly and L. G. J. Fokkink, *Langmuir*, **10**, 4089 (1994).
- W. Hoogsteen and L. G. J. Fokkink, *J. of Colloid and Interface Science* **175** 12 (1995).

To our knowledge no paper refers to patterning polymer-stabilized catalytic particles using a similar method to ours.

(G) Are there other contemplated forms of the invention or alternate aspects and uses?

(H) **Please List Proposed Claims.**

1. The use of a polymeric layer as a mask to pattern polymer-stabilised catalytic particles on a substrate.
2. Claim 1 where the catalytic particles are used to seed a ceramic, metal or polymer surface for subsequent electroless metallization.
3. Claim 1 where the masking material is such that polymer-stabilised seeding particles do not adsorb strongly to it, allowing the particles to be easily rinsed off with water or organic solvents.

4. Claim 1 where the polymeric mask material is a photosensitive polymer.
5. Claim 1 where the polymeric mask is patterned using a laser.
6. Claim 1 where a steric layer is used as the mask.
7. A method of selectively seeding materials on polymeric substrates. The material to be seeded and subsequently metallized is a material to which the particles adsorb. This material is patterned on a polymeric substrate to which the stabilised particles strongly adsorb.
8. Any preceding claim where the catalytic particles consist primarily of palladium.
9. Any preceding claim where the stabilising polymer is polyvinylpyrrolidone, poly-2-vinylpyridine or polyvinyl alcohol.
10. Any preceding claim where the stabilised sol is aqueous based.
11. Any preceding claim where the material to be selectively plated is indium-tin oxide (ITO).
12. Any preceding claim where the polymer to which the seeding particles do not strongly adsorb is polycarbonate, cellophane, polyimide or acrylate based or where it is a fluorinated polymer.

CONFIDENTIAL

Novel patterning method for selective metallization

CERTIFICATION

I, Peter Malcolm Moran, hereby certify that the invention entitled __, invention disclosure no. _____, (to be filled in by Admin. Officer-in-charge (Business Development), was made by me on 19/4, 2000, while I was employed at Institute of Materials Research and Engineering, while employed as a Research Fellow (Title of Position). The other inventor(s) were Sunil Madhukar Bhangale and Li Zhongli

The invention was made:

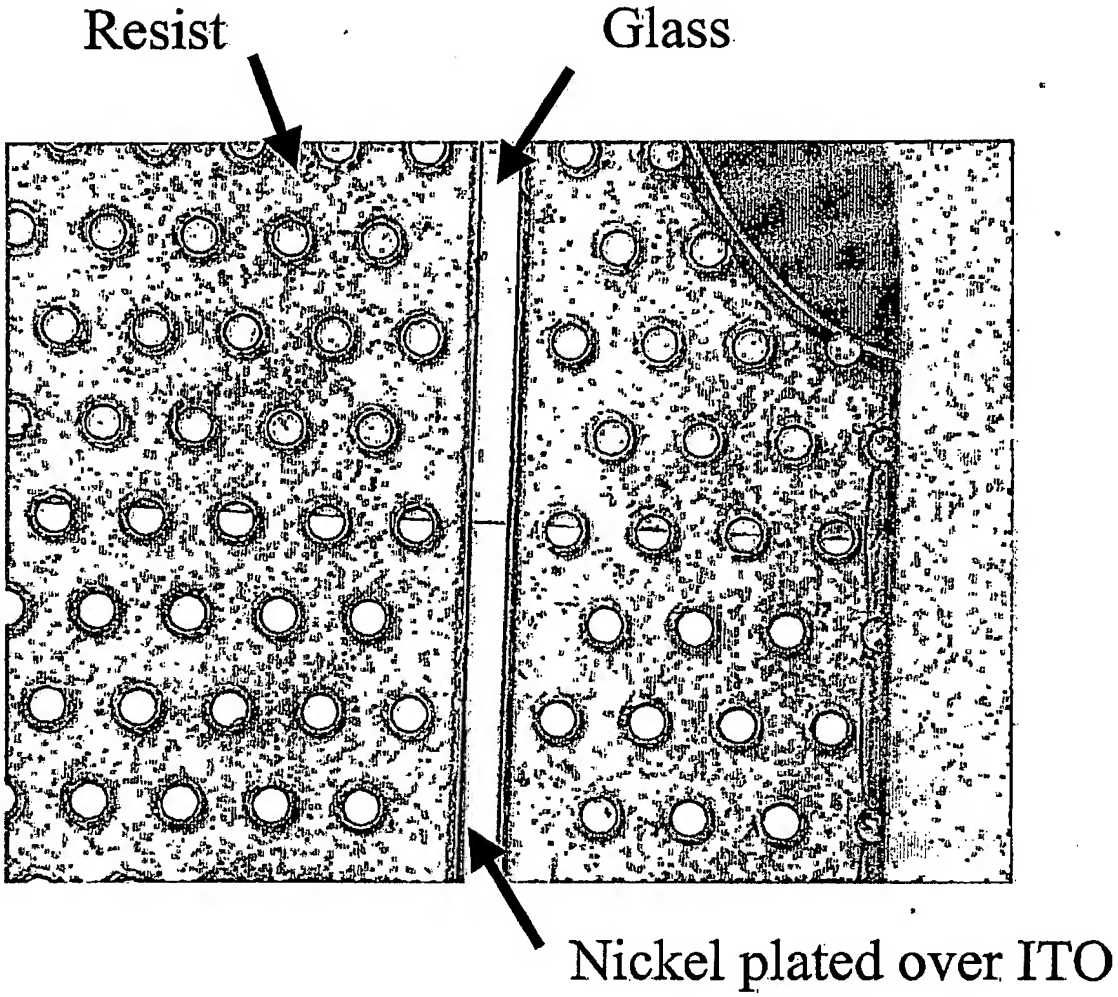
1.	During official working hours	Yes
2.	With a contribution by IMRE of:	
	(a) Facilities	Yes
	(b) Equipment	Yes
	(c) Materials/consumables	Yes
	(d) Funds	Yes
	(e) Information	Yes
	(f) My time or services while on official duty	Yes
	(g) Time or services of other IMRE employees on office duty	Yes
3.	The invention:	
	(a) Bears a direct relation to my official duties	Yes
	(b) Was made in consequences of my official duties	Yes
4.	I am attaching remarks relating to the above	

Signature: _____ 09 MAY 2001
(Programme Director)

Signature: _____ Peter Moran
(Inventor)

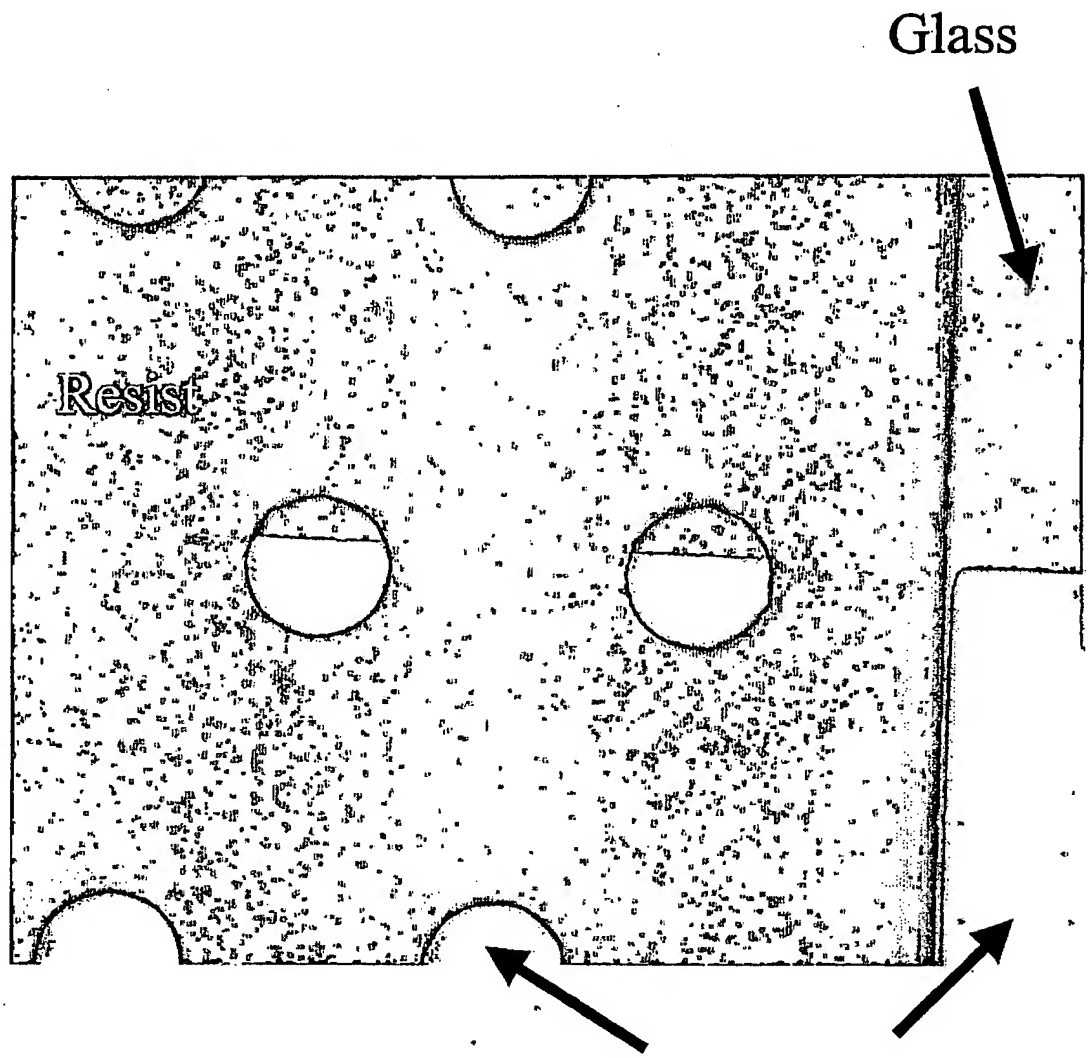
Present Title: Senior Research Fellow

Home address: #04-08 Tower 3B
West Cove Condos
10 West Coast Crescent
Singapore 128041



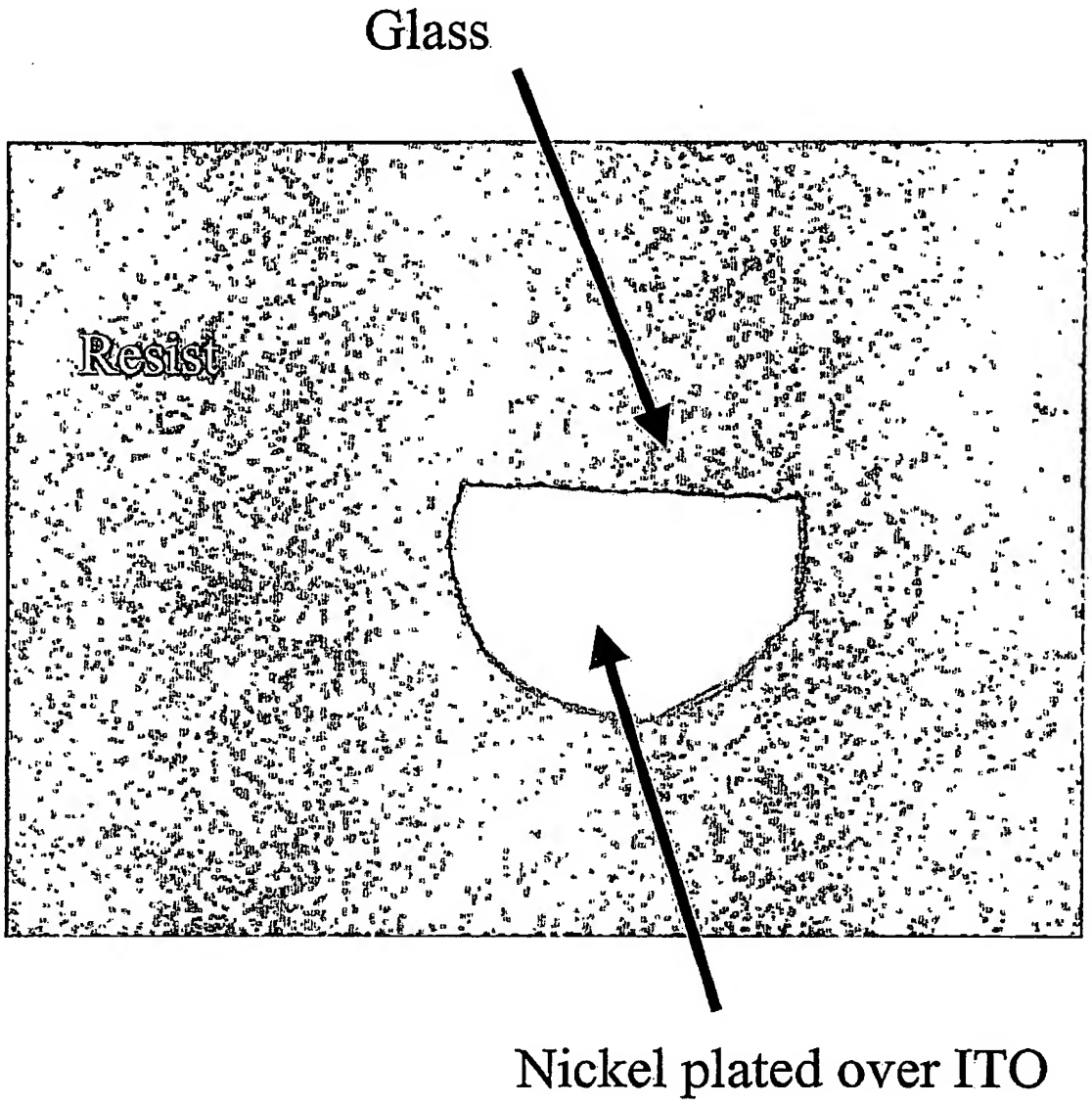
(Resist holes are about 125 μm in diameter)

Figure 1 Optical microscope image showing electroless nickel plated through a photoresist mask.



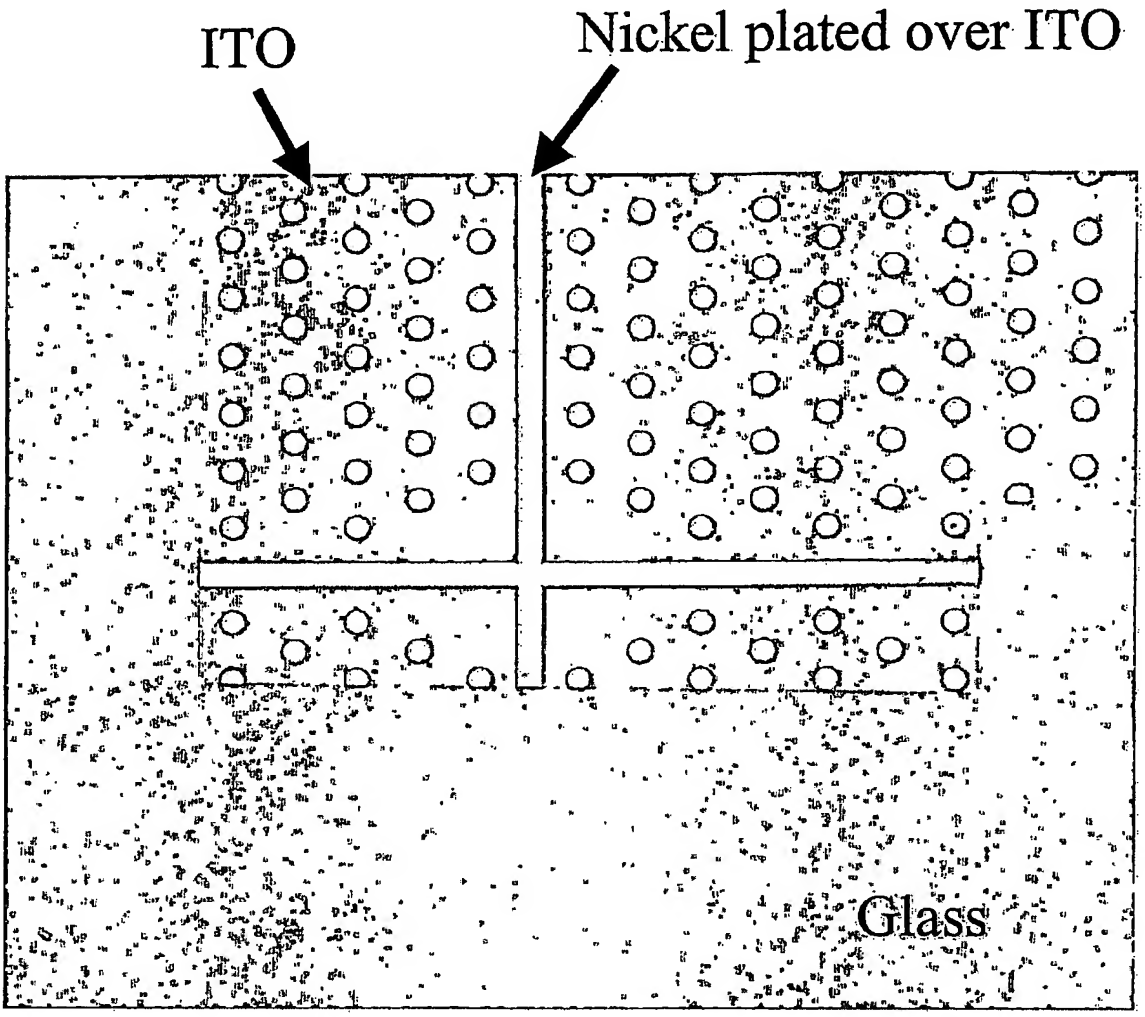
(Resist holes are about 125 μm in diameter)

Figure 2 Optical microscope image showing electroless nickel plated through a photoresist mask



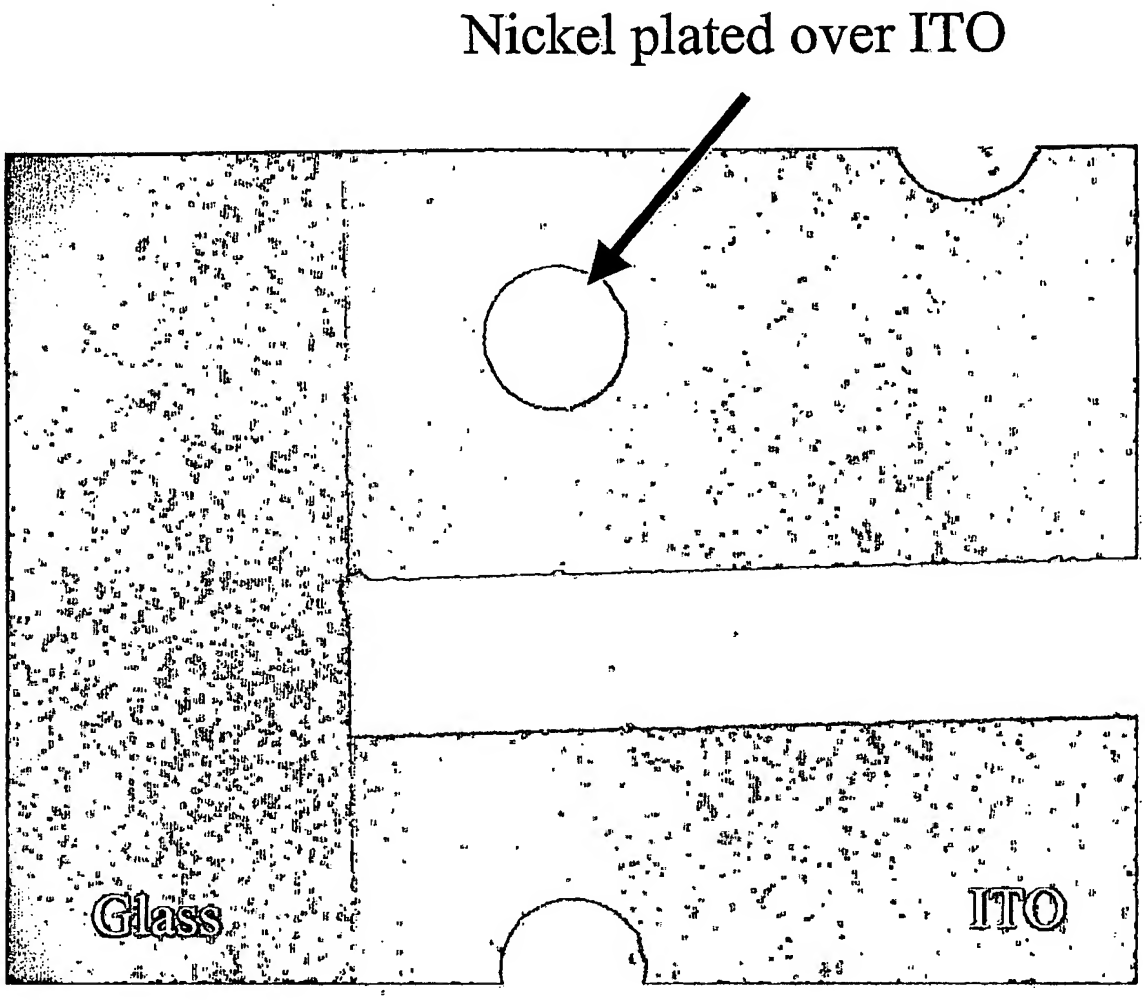
(Resist hole is about 125 μm in diameter)

Figure 3 Optical microscope image showing electroless nickel plated through a photoresist mask



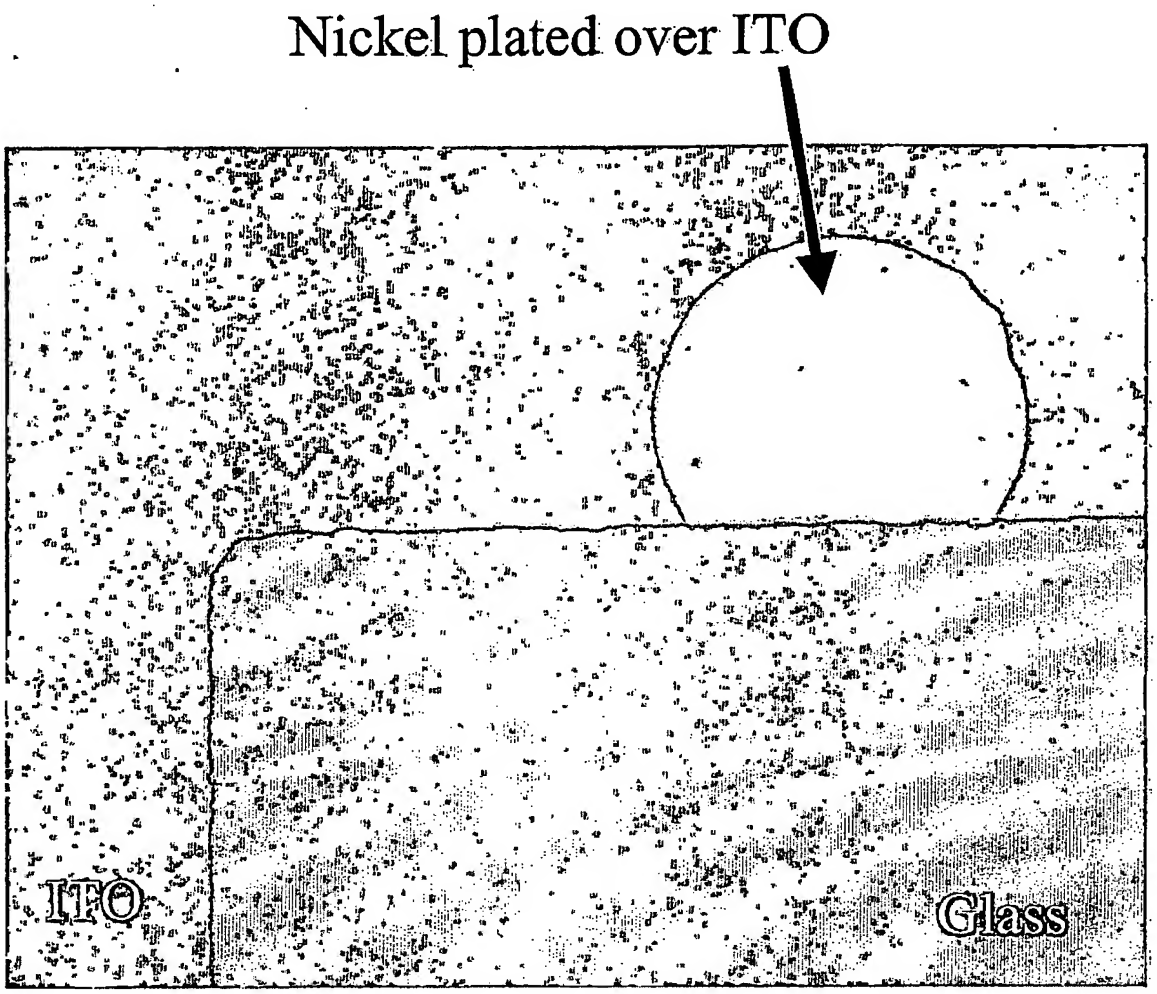
(Plated Ni circles are about 125 μm in diameter)

Figure 4 Optical microscope image showing plated electroless nickel selectively plated on ITO after the photoresist mask has been removed



(Plated Ni circles are about 125 μm in diameter)

Figure 5 Optical microscope image showing plated electroless nickel selectively plated on ITO after the photoresist mask has been removed



(Plated Ni circle is about 125 μm in diameter)

Figure 5 Optical microscope image showing plated electroless nickel selectively plated on ITO after the photoresist mask has been removed